# ZINC DEPOLARIZED ELECTROCHEMICAL CO<sub>2</sub> CONCENTRATION

# FINAL REPORT

by

R. R. Woods, R. D. Marshall

and F. H. Schubert

# October, 1975

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# AMES RESEARCH CENTER

**National Aeronautics & Space Administration** 

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# ZINC DEPOLARIZED ELECTROCHEMICAL CARBON DIOXIDE CONCENTRATION

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Prepared Under Contract No. NAS2-6478

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#### **FOREWORD**

The development and analysis work described herein was conducted by Life Systems, Inc. during the period of February, 1975 to October, 1975 under NASA Contract NAS2-6478. The Program Manager was R. D. Marshall. Technical support was provided by R. R. Woods and F. H. Schubert.

Direct technical monitorship was provided at NASA Ames Research Center, Moffett Field, California by Mark Leban. The program Technical Monitor was P. D. Quattrone, Chief, Environmental Control Research Branch, NASA Ames Research Center.

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#### SUMMARY

Two Zinc Depolarized Electrochemical Carbon Dioxide Concentrator (ZnDC) concepts were analytically and experimentally evaluated for Portable Life Support System (PLSS) carbon dioxide (CO2) removal application. The first concept, referred to as the Zinc Hydrogen Generator/Electrochemical Depolarized CO, Concentrator (ZHG/EDC), uses a ZHG to generate hydrogen  $(H_2)$  for direct use in an EDC. second concept, referred to as the Zinc/Electrochemical Depolarized Concentrator (Zn/EDC), uses a standard EDC cell construction modified for use with the Zn anode. The Zn anode is consumed and subsequently regenerated, thereby eliminating the need to supply H2 to the EDC for the CO2 removal process. The evaluation was based primarily on an analytical evaluation of the two ZnDCs at projected end-item performance and hardware design levels. The experimental data was used only to determine operational feasibility of the two concepts as regenerable CO<sub>2</sub> Both ZnDC concepts for PLSS CO2 removal application were found to be noncompetitive in both total equivalent launch weight and individual extravehicular activity (EVA) mission volume when compared to other candidate regenerable PLSS CO, scrubbers. As a result, further development work on the ZnDC concepts was not recommended.

Evaluation of the ZHG/EDC concept for PLSS application resulted in an eight-hour EVA volume of 3.0 x  $10^{-2}$  m  $^{3}$  (1.07 ft  $^{3}$ ) and a mass of 37.8 kg (83.3 lb). The ZHG/EDC Design evaluated used a 16-cell advanced EDC module capable of removing 119 g CO $_{2}$  per hour at an efficiency of 92% while producing 62.5W of power, and a 24-cell ZHG module which produces 8.7 g of H $_{2}$  per hour while generating an average of 53.9W of power. The total equivalent launch weight was 234 kg (515 lb) per man for a total of 1000 EVA mission hours, including expendables and weight penalties associated with the recharge system. Evaluation of the Zn/EDC concept for PLSS application resulted in a subsystem EVA volume of 2.4 x  $10^{-2}$  m  $^{3}$  (0.85 ft  $^{3}$ ) and an EVA mass of 26.7 kg (58.8 lb). The ZN/EDC design evaluated used a 16-cell Zn/EDC module capable of removing 119 g CO $_{2}$  per hour at an efficiency of 92% while producing 109.3W of power. The total equivalent launch weight was 237 kg (522 lb) per man for 1000 EVA hours, including expendables and weight penalties associated with the recharge system.

A single-cell and a five-cell ZHG module were designed, fabricated and tested to experimentally determine ZHG operational feasibility. Testing included the effect of current density on both the discharge (H<sub>2</sub> evolution) mode and the recharge mode. The five-cell ZHG module demonstrated an average single-cell voltage of 0.25V at 10 mA/cm² and 295 K (72F), and produced 1.5 times the stoichiometric-in-current H<sub>2</sub> requirement for a single-cell EDC as demonstrated during integrated ZHG/EDC operation. During the integrated testing, EDC performance was not affected by the ZHG-generated H<sub>2</sub>.

A single-cell Zn/EDC was designed, fabricated and tested. The cell, however, failed to operate as designed with cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>) electrolyte. When charged with cesium hydroxide (CsOH) electrolyte, the Zn/EDC demonstrated an

operational voltage of 1.24V at 21.5 mA/cm<sup>2</sup> and 295 K (72F) until the CO<sub>2</sub> content of the electrolyte increased and caused degradation of electrical performance. Further development work would be required to determine the mechanism by which the cell failed to operate and whether the concept could be made operationally feasible.

#### INTRODUCTION

As the lengths of manned space missions increase, more ambitious extravehicular activities (EVAs) will be attempted. Current state-of-the-art Portable Life Support Systems (PLSS) involve the use of expendables, but for the projected longer missions these expendables will become prohibitive due to increased weight and volume penalties. The removal of metabolically-generated carbon dioxide (CO<sub>2</sub>) in a PLSS is currently performed using expendable chemicals (i.e., lithium hydroxide (LiOH)). The development of a regenerable CO<sub>2</sub> scrubber for PLSS application is, therefore, desirable. A regenerable Zinc Depolarized Electrochemical CO<sub>2</sub> Concentrator (ZnDC) concept was a potential candidate to perform this CO<sub>2</sub> scrubbing function.

#### Background

Two ZnDC concepts were identified for PLSS application. The first concept, referred to as the Zinc Hydrogen Generator/Electrochemical Depolarized CO<sub>2</sub> Concentrator (ZHG/EDC), is a regenerable ZHG integrated with an EDC. The EDC is an advanced electrochemical CO<sub>2</sub> removal device developed by Life Systems, Inc. (LSI) in which CO<sub>2</sub> is removed from the process air and is regenerated into a hydrogen (H<sub>2</sub>) stream. During operation, the EDC consumes oxygen (O<sub>2</sub>) and H<sub>2</sub> while producing water, heat and electrical power. The ZHG is a cyclically-regenerable battery which produces H<sub>2</sub> gas, power and heat when discharged. The function of the ZHG is to produce 1.5 times the stoichiometric-in-current H<sub>2</sub> requirement of the EDC. When integrated, the ZHG and EDC require only process air, coolant and a power controller to perform the CO<sub>2</sub> removal function.

The second concept, referred to as the Zinc/Electrochemical Depolarized CO $_2$  Concentrator (Zn/EDC), uses the standard EDC cell construction modified for use with the Zinc (Zn) anode. The construction of the cell is similar to a Zn/air battery. During the discharge mode, Zn and O $_2$  are consumed to perform the CO $_2$  removal function, and electrical energy and waste heat are produced. The Zn/EDC requires only process air, coolant and a power controller to perform the CO $_2$  removal function. The Zn electrode and O $_2$  consumed during the EVA are regenerated onboard the primary space vehicle. The advantage of the Zn/EDC over the ZHG/EDC concept for PLSS application is the elimination of H $_2$  gas within the CO $_2$  removal process.

<sup>(1)</sup> All references cited in parentheses are listed on page 54.

#### Program Objectives and Organization

The object of the present program was to evaluate the ZHG/EDC and Zn/EDC concepts for PLSS application. Concept evaluation consisted of feasibility testing of a ZHG/EDC and a Zn/EDC for operability as opposed to establishing state-of-the-art design data, and analytically determining end-item application feasibility at projected performance and hardware design levels for comparison to alternate PLSS CO<sub>2</sub> removal concepts.

To accomplish the program objective, the program was divided into three tasks, and program documentation and management functions. The specific objectives of the three tasks were to:

- 1. Design, fabricate and test a ZHG module and integrated ZHG/EDC to determine if the ZHG/EDC concept is operable.
- 2. Design, fabricate and test a Zn/EDC to determine if the Zn/EDC concept is operable.
- 3. Review and establish the PLSS CO<sub>2</sub> scrubber specifications and analytically evaluate the two ZnDC concepts for PLSS application.

The objectives of the program were met. The following sections summarize the work completed, and the conclusions and recommendations reached.

#### ZHG/EDC CONCEPT

A block diagram of the ZHG/EDC CO<sub>2</sub> Removal Subsystem, as integrated within a PLSS, is presented in Figure 1. Figure 1 depicts the atmospheric revitalization loop, the liquid coolant loop and the controller connections to the various subsystems of the PLSS. The EDC is the second subsystem in the atmospheric revitalization loop. The inlet process air to the EDC is warm, moist and debris-free, while the ZHG has no direct contact with the atmospheric loop. Both the ZHG and EDC place loads on the heat rejection subsystem while requiring connections to the PLSS controller. The EDC also increases the water content of the process air due to the production of water in the electrochemical cell reactions.

#### Zinc Hydrogen Generator Process Description

The ZHG is simply a  $\rm Zn/O_2$  battery discharged into an O<sub>2</sub> deficient atmosphere. The electrochemical cell discharge reactions are summarized in Table 1. At the cathode, where the O<sub>2</sub> is normally reduced to form hydroxyl ions (OH ) in a  $\rm Zn/O_2$  battery, two water molecules are reduced in the ZHG to form two OH plus one molecule of H<sub>2</sub>. The OH transfer to the anode where Zn is oxidized and the Zn electrode consumed. The theoretical discharge voltage is 0.388V and at a feasible operating current density the system will produce power.

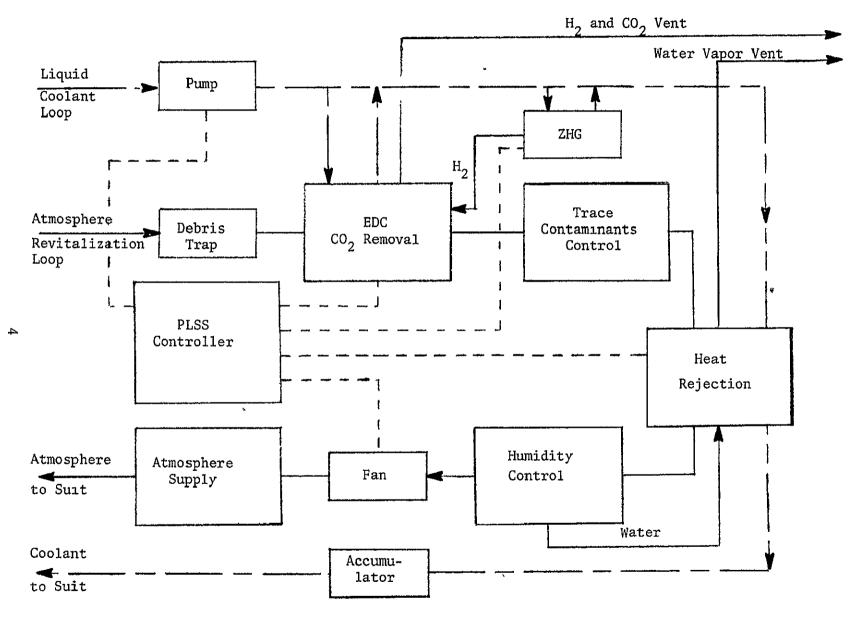


FIGURE 1 PLSS BLOCK DIAGRAM FOR ZHG/EDC CONCEPT

# TABLE 1 ZHG ELECTROCHEMICAL DISCHARGE REACTIONS (a)

CATHODE

$$2H_2O + 2e^- = 2OH^- + H_2$$
 (1)

ANODE

$$Zn + 20H = Zn0 + H_20 + 2e$$
 (2)

$$Zn + 2OH^- = Zn(OH)_2 + 2e^-$$
 (3)

$$Zn + 4OH^- = Zn(OH)_4^- + 2e^-$$
 (4)

**OVERALL** 

$$Zn + H_2O = ZnO + H_2$$
 (5)

$$Zn + 2H_2O = Zn(OH)_2 + H_2$$
 (6)

$$Zn + 2H_2O + 2OH^- = Zn(OH)_4^- + H_2^-$$
 (7)

<sup>(</sup>a) Recharge reactions are the reversal of the discharge reactions.

<sup>(</sup>b) Reaction (5) is the sum of reactions (1) and (2).

<sup>(</sup>c) Reaction (6) is the sum of reactions (1) and (3).

<sup>(</sup>d) Reaction (7) is the sum of reactions (1) and (4).

The electrochemical cell recharge reactions are simply the reverse of discharge reactions presented in Table 1. Cell recharge is accomplished by reversing the current flow through the cell (i.e., the Zn electrode becomes the cathode and the screen electrode becomes the anode). Hydrogen gas is introduced at the cell recharge anode where it is oxidized in the presence of OH to form water. The water produced is then absorbed into the electrolyte to replenish water consumed during discharge. At the cathode, the Zn oxide (ZnO) formed during discharge is reduced to reform the Zn electrode and produce OH which transfer through the cell to the anode for consumption. The theoretical recharge voltage is 0.388V and the recharge process requires electrical power.

#### Hardware Description

The module used for the ZHG/EDC concept feasibility testing is a modified commercially-available Zn/O<sub>2</sub> battery. A schematic of the ZHG single cell is presented in Figure 2. A photograph of a five-cell ZHG module is presented in Figure 3. Table 2 contains the ZHG cell components.

The anode is fabricated by reducing a mixture of the Zn oxide and mercury oxide (2%) onto a silver sheet current collector. This fabrication technique results in a high performance Zn electrode with good recharge capabilities. The cathode of the ZHG is a platinum (Pt) screen electrode plated on a teflon membrane. The teflon membrane is in contact with the module gas cavity and prevents electrolyte from leaking into the cavity. Two cathodes are integrated into each single-cell housing frame to provide activity to both sides of the Zn anode. The cathodes and cell housing frame create an envelope to contain the anode-matrix combination. The asbestos matrix is wrapped around the Zn anode and together they slip into the cell housing envelope. An O-ring seal is provided at the contact point between the cell housing frame and the anode, as illustrated in Figure 2.

Each cell is charged with 20 cm<sup>3</sup> of 30% KOH electrolyte. Five individual ZHG cells are integrated into the module and are electrically connected in series. Physical separation of the individual cells is provided by six pieces of stainless steel expanded metal while compression is provided by two tension rings which fit around the five-cell stack and are tightened with eight hex screws. This cell stack is then placed into the stainless steel module housing which is simply a sealed box. The module housing has a single port for gas flow, a removable screw to provide purge capabilities, and module current and voltage terminals.

#### Hydrogen Production Rate

The rate at which  $\mathrm{H}_2$  is produced by the ZHG is proportional to cell current. According to Faraday's Law, the  $\mathrm{H}_2$  production rate is given by the equation:

$$H = 1.04 \times 10^{-5} (N) (I) (\eta)$$
 (1)

where

 $H = H_2$  production rate, g/s

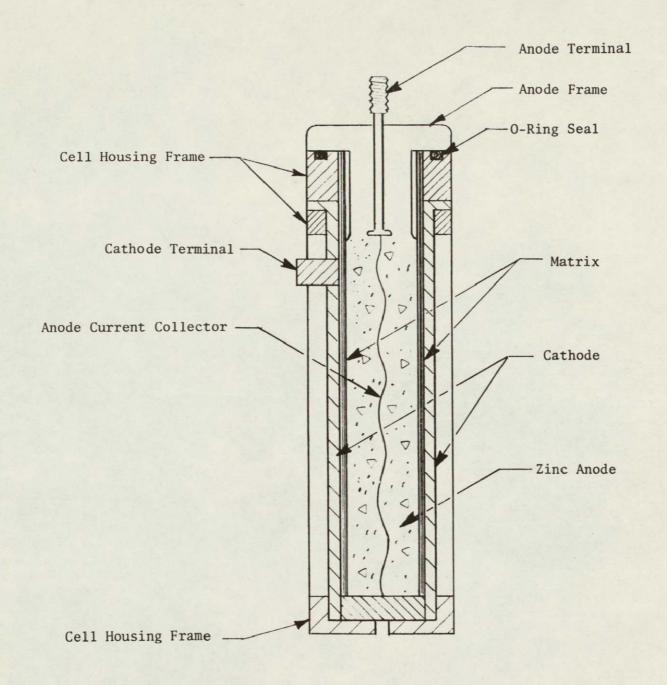


FIGURE 2 ZHG SINGLE-CELL SCHEMATIC

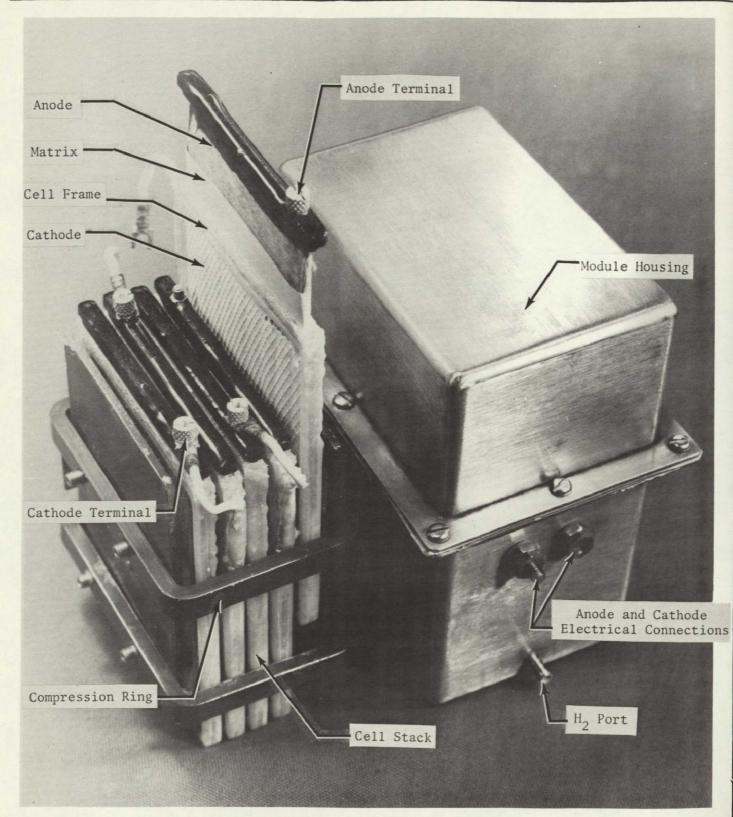


FIGURE 3 ZHG MODULE

TABLE 2 ZHG CELL COMPONENT CHARACTERISTICS

Configuration	ZHG No. 1	ZHG No. 2	ZHG No. 3
Active Area, cm <sup>2</sup> (Ft <sup>2</sup> )	150 (0.161)	51.6 (0.056)	147 (0.158)
Dimensions, cm (In)	7.1 x 10.5 (2.8 x 4.13)	4.3 x 6.0 (1.7 x 2.36)	7.0 x 10.5 (2.76 x 4.13)
Anode	Porous Zinc	Porous Zinc	Porous Zinc
Anode Thickness, cm (In)	0.25 (0.100)	0.081 (0.032)	0.076 (0.030)
Discharge Capacity, A-h	30	1.56	8.1
Matrix	Asbestos	Asbestos	Asbestos
Matrix Thickness, cm (In)	0.020 (0.008)	0.076 (0.030)	0.076 (0.030)
Cathode	Platinum Screen on Teflon	Platinum Screen on Teflon	Platinum Screen on Teflon
Cathode Thickness, cm (In)	0.010 (0.004)	0.010 (0.004)	0.010 (0.004)
Anode Frame	Epoxy Resin	Silicon Rubber	Silicon Rubber
Cell Housing Frame	Polysulfone	Polysulfone	Polysulfone
Anode Current Collector	Silver Plated Screen	Silver Sheet	Silver Sheet
O-Ring	Ethylene Propylene	Not Used	Not Used

N = Number of series connected cells

I = Cell current, A

η = Current efficiency, fraction of unity
 (η during discharge = 1)

Using the ideal gas law, the volumetric H2 flow rate is given by the equation:

$$V_{H_2} = 4.32 \times 10^{-8} (N)(I)(T)(\eta)$$
 (2)

where

 $V_{H_2} = H_2 \text{ production, } m^3/s$ 

T = Temperature, K

 $P = Pressure, kN/m^2$ 

The above equations are applicable for both the discharge and recharge modes.

### Zinc Oxidation and Reduction Rates

In the discharge or  $\rm H_2$  generation mode, the Zn anode is oxidized to form a Zn oxide. In the recharge mode, current is reversed and the Zn oxide is reduced to reform the Zn electrode. According to Faraday's Law, the rate of Zn oxidation or reduction is given by the equation:

$$Z = 3.39 \times 10^{-4} (N) (I) (\eta)$$
 (3)

where

Z = Zn oxidation or reduction rate, g/s

#### Power Production and Consumption Rate

The ZHG module produces power during discharge and consumes power during recharge. The power produced during discharge or consumed during recharge is given by the equation:

$$P = (N)(I)(E)$$
 (4)

where

P = Power, W

E = Average cell voltage, V

#### Heat Generation Rate

The amount of heat generated by the ZHG in both the discharge and recharge modes is determined by the difference between the operating cell voltage and the theoretical cell voltage. For the discharge mode, where the current efficiency is one, the heat generation rate is given by the equation:

$$Q = (I)(N) E-E_{t}(n)$$
 (5)

where

Q = Heat produced, J/s

 $E_{t}$  = Theoretical cell voltage, V

During the recharge mode, where the current efficiency is below one, an additional heat generation equation is necessary. The heat produced due to the recharge current inefficiencies is given by the equation:

$$Q^1 = (I)(N)(E)(1-\eta)$$
 (6)

where

 $Q^1$  = Heat generated, J/s

Therefore, the total heat generated during recharge is given by the sum of Equations 5 and 6 above.

$$Q_{R} = (I) (N) E-E_{t} (\eta) + (I) (N) (E) (I-\eta)$$
(7)

where

 $Q_{\rm p}$  = Heat generated during recharge, J/s

#### Performance Parameters

The performance of the ZHG can be measured by four parameters: H<sub>2</sub> production efficiency, projected cycle life, average cell voltage and recharge current efficiency.

<u>Hydrogen Production Efficiency</u>. Since the function of the ZHG is to produce  $H_2$  gas for use in an EDC, the initial evaluation of ZHG performance involves the efficiency at which this  $H_2$  gas is produced. The efficiency of  $H_2$  production is the ratio of the measured  $H_2$  flow rate over the theoretical flow rate as calculated using Equation 1. Theoretically, there is no major inefficiency in the discharge mode and the current and  $H_2$  production efficiency are approximately equal to one during discharge.

Projected Cycle Life. The cycle life of the ZHG is determined by the number of discharge/recharge cycles which can be performed before the final discharge cell potential decreases to zero. As the ZHG is cycled, the total capacity of the Zn anode is decreased due to inefficiencies in recharge which prevent a portion of the Zn electrode from being reformed.

Average Cell Voltage. The ZHG average cell voltage affects the power and heat produced. During discharge, as average cell voltages decrease due to decreasing anode capacities, the power produced decreases while the heat generated is increased.

Recharge Current Efficiency. The ratio of the total current required during recharge and discharge represents the recharge current efficiency. During the recharge mode, the current efficiency is reduced by the electrochemical generation of H<sub>2</sub> at the cathode, which results in H<sub>2</sub> backdiffusion or H<sub>2</sub> leakage into the gas compartment for reconsumption at the anode. This mechanism results in the consumption of power without reforming the Zn electrode. The ratio evaluates quantitatively the amount of H<sub>2</sub> backdiffusion or leakage that occurs and is useful in determining the total amount of power required for the ZHG recharge.

Electrochemical Depolarized CO<sub>2</sub> Concentrator Process Description

Carbon dioxide is removed from a flowing air stream as it passes over the cathode of an EDC cell. Each cell consists of two porous electrodes separated by a porous matrix containing an aqueous solution of cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>). Plates adjacent to the electrodes provide passageways for distribution of the process gases and electrical current over the electrode surfaces. The specific electrochemical and chemical reactions are detailed in Table 3.

Moist air containing CO<sub>2</sub> is fed into the cathode where the electrochemical reaction of O<sub>2</sub> in the air, water and electrons forms OH . The CO<sub>2</sub> then reacts with the OH at the cathode to form CO<sub>3</sub>. The output from the cathode compartment is moist air at a reduced CO<sub>2</sub> partial pressure (pCO<sub>2</sub>). The CO<sub>2</sub> as CO<sub>3</sub> and unreacted OH diffuse through the bulk electrolyte to the anode, thereby transporting current and CO<sub>2</sub> through the cell.

At the anode,  $H_2$  is fed into the cell where it is electrochemically reduced in the presence of  $OH^-$  to form water and electrons, thereby decreasing the concentration of  $OH^-$  in the anolyte. The shift in anolyte pH causes  $CO_2$  to evolve at the anode. The output from the anode compartment is  $CO_2$  mixed with unreacted  $H_2$ . The water produced at the anode transfers to the cathode and evaporates into the process air. The overall reaction is exothermic and is accompanied by the formation of electrical energy.

## TABLE 3 EDC ELECTROCHEMICAL AND CHEMICAL REACTIONS

CATHODE

$$0_2 + 2H_2O + 4e^- = 40H^-$$
  
 $40H^- + 2CO_2 = 2H_2O + 2CO_3^=$ 

ANODE

$$2H_2 + 40H^2 = 4H_2O + 4e^2$$
  
 $2CO_3^2 + 2H_2O = 2CO_2 + 40H^2$ 

OVERALL

$$0_2 + 2C0_2 + 2H_2 = 2C0_2 + 2H_20 + Electrical Energy + Heat$$

#### Hardware Description

The EDC cell used in the evaluation of the Zn concept is a LSI liquid-cooled cell configuration. Figure 4 is a schematic of the EDC cell. The cell consists of a cathode and anode gas compartment, two current collectors with gas compartment spacers, two electrodes and an electrolyte matrix. The basic materials of construction are LSI baseline electrodes, asbestos electrolyte matrix, nickel (Ni) expanded metal gas compartment spacers, Ni current collectors and polysulfone structural cell frames. The cell has internal liquid cooling adjacent to the cathode gas cavity to remove the waste heat generated by the electrochemical reactions. The materials of construction and cell dimensions are summarized in Table 4.

#### Gas Consumption Rates

During EDC operation,  $H_2$  and  $O_2$  gases are consumed to produce the  $OH^-$  ions needed for the  $CO_2$  removal process. According to Faraday's Law the gas consumption rates are given by the equations:

$$0' = 8.3 \times 10^{-5} (I')(N')$$
 (8)

where

 $0' = EDC O_2$  consumption rate, g/s

I = EDC current, A

N = Number of EDC cells

$$H' = 1.04 \times 10^{-5} (I')(N')$$
 (9)

where

H = EDC H<sub>2</sub> consumption\_rate, g/s

#### Water Generation Rate

During EDC operation, water is produced according to the equation:

$$W' = 9.33 \times 10^{-5} (I')(N')$$
 (10)

where

W = Water production rate, g/s

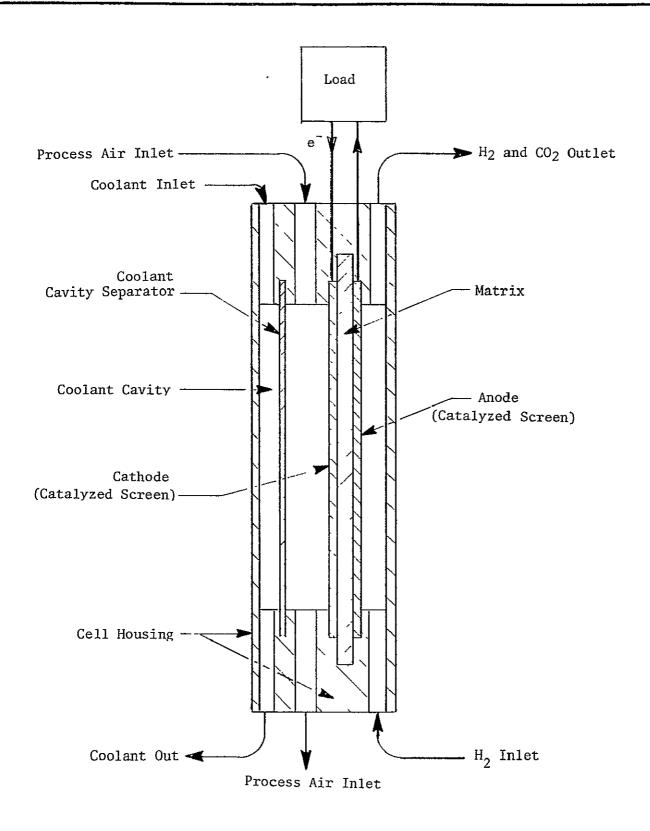


FIGURE 4 LIQUID-COOLED EDC SCHEMATIC

#### TABLE 4 EDC CELL COMPONENT CHARACTERISTICS

		2	·- 2.
Active	Area,	cm	(Ft <sup>-</sup> )

Dimensions, cm (In)

Anode

Anode Thickness, cm (In)

Cathode

Cathode Thickness, cm (In)

Matrix

Matrix Thickness, cm (In)

Coolant Cavity Separator

Cell Housing Frames

Air Cavity Height, cm (In)

H<sub>2</sub> Cavity Height, cm (In)

Coolant Cavity Height, cm (In)

Gas Cavity Spacers

Current Collectors

Gaskets

227 (0.244)

10.4 x 21.8 (4.1 x 8.6)

LSI Catalyzed Screen

0.025 (0.010)

LSI Catalyzed Screen

0.025 (0.010)

Asbestos

0.076 (0.030)

Polysulfone

Injection-Molded Polysulfone

0.208 (0.082)

0.157 (0.062)

0.165 (0.065)

Nickel 200

Nickel 200

Ethylene Propylene

#### Power and Heat Produced

The power and heat produced by the EDC during operation are described by the same equations used for the ZHG discharge mode, Equations 4 and 5. The current efficiency of the EDC operation is one.

#### Performance Parameters

The performance of an EDC is reflected by  ${\rm CO}_2$  removal efficiency and electrical efficiency.

Carbon Dioxide Removal Efficiency. Inspection of the overall reaction as based on the  $\mathrm{CO_3}^=$  transfer mechanism shows that two moles of  $\mathrm{CO_2}$  can be transferred for one mole of  $\mathrm{O_2}$  consumed. This represents a  $\mathrm{CO_2}$  removal efficiency of 100%. The equivalent mass ratio is 2.75 kg of  $\mathrm{CO_2}$  removed for each kg of  $\mathrm{O_2}$  consumed. This ratio is referred to as the Transfer Index (TI).

Electrical Efficiency. The electrical energy produced by the electrochemical reaction in the EDC is a function of the current density and the cell voltage. The theoretical open-circuit voltage is 1.23V. In practical applications and with current flowing, cell voltages of less than 1.23V result. Electrical efficiency is, therefore, reflected by cell voltage with high cell voltage representing high electrical efficiency.

#### Ground Support Accessories

During testing of the ZHG/EDC, the Ground Support Accessories (GSA) were utilized to provide the following functions:

- 1. Fluid interfaces
- 2. Electrical power
- Monitoring of engineering parameters
- 4. Protective shutdown circuits with indication lights

#### Zinc Hydrogen Generator Ground Support Accessories

A schematic of the GSA for ZHG operation is provided in Figure 5. The GSA provided load control for the discharge mode and H<sub>2</sub> flow and power for the recharge mode. The GSA contained instrumentation for the measurement of H<sub>2</sub> temperature, dew point, pressure and flow rate, and module current and voltage. Hydrogen dew point was measured using a Cambridge Model 880 Hygrometer. A soap bubble flow meter was used for accurate H<sub>2</sub> flow measurements. The protective shutdown circuitry was designed to provide a low voltage shutdown during discharge and a high voltage shutdown during recharge.

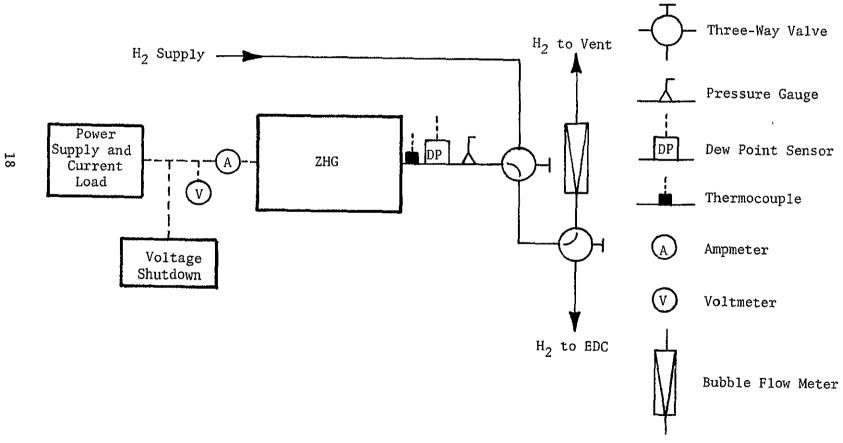


FIGURE 5 ZHG TEST FACILITY SCHEMATIC

# Electrochemical Depolarized CO<sub>2</sub> Concentrator Ground Support Accessories

The GSA schematic for the EDC is shown in Figure 6. The GSA has the capability of varying inlet pCO<sub>2</sub> level, process air, inlet dew point and flow rate, H<sub>2</sub> flow rate, current and inlet liquid coolant temperature. Inlet and outlet air dew points were measured using a Cambridge Model 880 Hygrometer. Accurate flow measurements were obtained using a soap bubble flow meter and a wet test meter. Inlet and outlet air pCO<sub>2</sub> levels were measured using Lira Model 300 CO<sub>2</sub> Infrared Analyzer for CO<sub>2</sub> in air (0 to 0.5% CO<sub>2</sub> at full scale). Anode gas pCO<sub>2</sub> levels were measured by Lira Model 300 CO<sub>2</sub> Infrared Analyzer for CO<sub>2</sub> in H<sub>2</sub> (0 to 100% CO<sub>2</sub> and H<sub>2</sub> at full scale). The test facility provided for 15w EDC voltage shutdown.

#### ZHG/EDC Test Program

The ZHG/EDC test program was designed to determine if the ZHG/EDC concept was operable as a potential CO<sub>2</sub> scrubber for PLSS application. The program was divided into three major areas of investigation: effect of current density on ZHG performance, ZHG cycle testing and ZHG/EDC integrated testing. The current density evaluation included experimental characterization of three different single-cell ZHG configurations, each using a different Zn anode and designated as ZHG configuration Number 1, 2 and 3. Cycle tests were performed on both the single and five-cell levels. Zinc Hydrogen Generator configuration Number 2 was used in single-cell cycle tests, while ZHG configuration Number 3 was used in the five-cell module. The integrated testing was performed with the five-cell ZHG module, which provided the 1.5 stoichiometric-in-current H<sub>2</sub> requirements for a single-cell EDC. Baseline test conditions for the ZHG and EDC are presented in Table 5.

#### Current Density Tests

The effect of current density on ZHG performance was measured for both the discharge and recharge modes.

Objective. The objective of the current density testing was to determine ZHG operational feasibility and to select discharge and recharge current density levels for the cyclic operation.

Procedure. The procedure followed during the ZHG current density testing was:

- 1. The single-cell ZHG was assembled and charged with 30% KOH.
- 2. Zinc  $H_2$  Generator Numbers 1 and 3 were discharged for 30 minutes at 10 mA/cm $_2$  (9.3 ASF). Zinc  $H_2$  Generator Number 2 was discharged at 10 mA/cm $_2$  (9.3 ASF) until 20% of the total anode discharge capacity was reached (36 minutes).

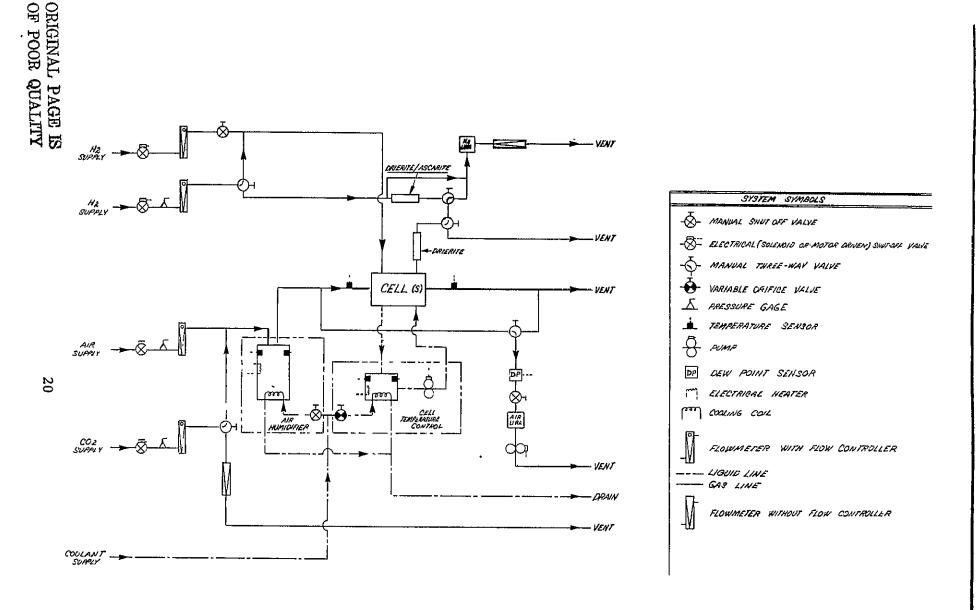


FIGURE 6 EDC AND Zn/EDC TEST FACILITY SCHEMATIC

TABLE 5 ZHG/EDC BASELINE CONDITIONS

# Zinc H<sub>2</sub> Generator

Current Density, mA/cm <sup>2</sup> (ASF)	
Discharge Recharge	10 (9.3) 10 (9.3)
H <sub>2</sub> Flow, cm <sup>3</sup> /m.	
Discharge - EDC Cell <sup>(a)</sup> Recharge	56 90 ±10
Stoichiometric H <sub>2</sub> Flow Cell Temperature, K (F)	1.5 295 ±2 (72 ±4)
Electrolyte	КОН
Charge Concentration, %	30
Capacity Discharge, %	30 ±2

## Electrochemical Depolarized Concentrator

Air Flow Rate, m <sup>3</sup> /s (Scfm) (a)	$2.8 \pm 0.2 \times 10^{-4}$
pCO <sub>2</sub> , N/m <sup>2</sup> (mm Hg) Inlet RH, %	(0.60 ±0.04) 400 (3)
Inlet RH, %	65 ±5
Inlet Process Air Temperature, K (F)	294 ±3 (70 ±5)
Cell Temperature, K (F)	295 ±3 (72 ±5)
Cooling Water Flow Rate, cm <sup>3</sup> /m	500
Current. A	4.88
Current Density, mA/cm <sup>2</sup> (ASF)	21.5 (20)
Electrolyte	Cs <sub>2</sub> CO <sub>3</sub>
Charge Concentration, %	61.5
Charge Concentration, % Pressure, kN/m² (mm Hg)	97.3 ±1.3
	(730 ±10)

<sup>(</sup>a) Standardized to 101.3 kN/m $^2$  (760 mm Hg) and 294K (70F)

- 3. For ZHG Numbers 1 and 3, the current density was increased to 20 mA/cm<sup>2</sup> (18.6 ASF) and the cells discharged<sub>2</sub> for 30 minutes. Zinc H<sub>2</sub> Generator Number 2 was discharged at 20 mA/cm<sup>2</sup> (18.6 ASF) until 40% of the total anode discharge capacity was reached (18 minutes).
- 4. For ZHG Numbers 1 and 3, the current density was increased to 30 mA/cm<sup>2</sup> (27.9 ASF) and the cells discharged for 30 minutes. Zinc H<sub>2</sub> Generator Number 2 was discharged at 30 mA/cm<sup>2</sup> (27.9 ASF) until 60% of the total anode discharge capacity was reached (12 minutes).
- 5. The single-cell ZHGs were recharged by a similar procedure at 5 mA/cm<sup>2</sup> (4.6 ASF), 10 mA/cm<sup>2</sup> (9.3 ASF) and 15 mA/cm<sup>2</sup> (13.9 ASF). Zinc H<sub>2</sub> Generator Numbers 1 and 3 were held at each current density level for 30 minutes, while ZHG Number 2 was held at each current density level for 10% of the total anode discharge capacity.
- 6. At the completion of the 15 mA/cm<sup>2</sup> (13.9 ASF) recharge, the current density was lowered to 10 mA/cm<sup>2</sup> (9.3 ASF) and recharging continued until rapidly increasing terminal voltages indicated a complete recharge.

Results. The results of the ZHG current density evaluations are presented in Figure 7 which illustrates terminal recharge and discharge voltage versus current density. The specific test conditions are given in Table 6. All three ZHG configurations produced power during the discharge mode at all three current densities. Zinc H<sub>2</sub> Generator Number 2 demonstrated the best performance during the current density testing. It illustrated a 0.325, 0.245 and 0.205V level at respective current density levels of 10, 20 and 30 mA/cm (9.3, 18.6 and 27.9 ASF). It also demonstrated a lower recharge terminal voltage at each recharge current density.

Although the ZHG Number 1 performed normally during the discharge mode, upon recharge the cell voltage was below the theoretical recharge voltage of 0.388V, indicating that an alternate electrochemical reaction occurred. It is believed that the alternate reaction was a generation of H $_2$  gas at the Zn electrode followed by the diffusion through the cell matrix or leakage around the O-ring seal to the H $_2$  cavity. Upon disassembly, visual observation verified that regeneration of the Zn electrode did not occur. The presence of an adsorbed H $_2$  on the surface of the Zn electrode was observed by its reaction with O $_2$  in the ambient air which caused the electrode to heat up.

In ZHG Numbers 2 and 3, H<sub>2</sub> evolution was also believed to be the cause of observed recharge inefficiencies. In both cases, more current was required than the stoichiometric amount necessary to regenerate the Zn anode. For ZHG Number 2, approximately 50% more amp-hours were consumed on recharge than produced during discharge; ZHG Number 3 required only 10% more.

#### Cyclic Operation

A single-cell ZHG and a five-cell ZHG was tested for 10 and 7 cycles, respectively.

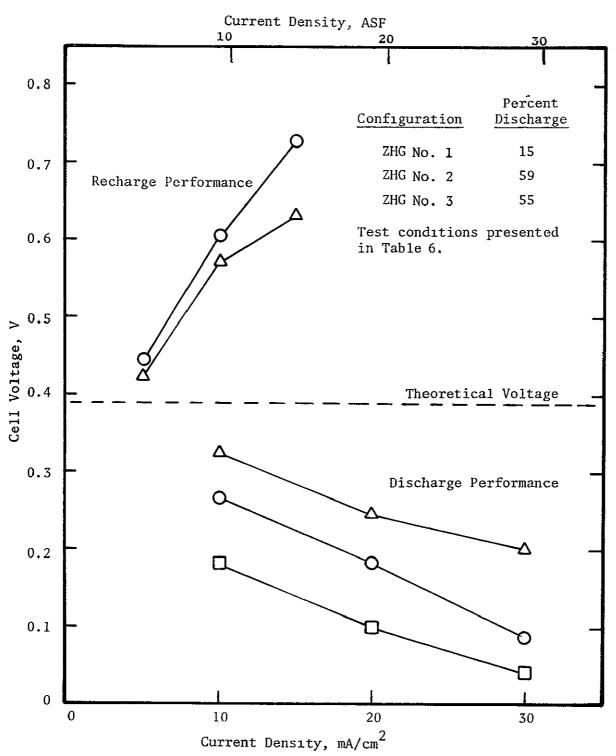


FIGURE 7 ZHG CURRENT DENSITY PERFORMANCE COMPARISON OF ZHG NOS. 1, 2, AND 3

TABLE 6 ZHG SINGLE-CELL TEST PARAMETERS

Configuration	ZHG No. 1	ZHG No. 2	ZHG No. 3
Number of Cells	1	1	1
Cell Active Area, $cm^2$ (Ft $^2$ )	150 (0.161)	51.6 (0.056)	147 (0.158)
Cell Capacity, A-h	30	1.56	8.1
Electrolyte	30% KOH	30% KOH	30% KOH
Current Density, mA/cm <sup>2</sup> (ASF)			
Discharge	Variable	Variable	Variable
Recharge	Variable	Variable	Variable
Cell Temperature, K (F)			
Discharge	296 (73)	295 ±2 (72 ±4)	294 ±1 (70 ±2)
Recharge	296 (73)	294 ±2 (70 ±4)	294 ±1 (70 ±2)
Depth of Discharge, %	15	59	55
Recharge H <sub>2</sub> Flow, cm <sup>3</sup> /min	163	100	74
Recharge H <sub>2</sub> Dew Point, K (F)	293 (68)	291 ±1 (65 ±2)	292 (66)

Objective. The objective of the cyclic operation was to verify the ability of the ZHG to produce  $\rm H_2$  and power as a function of multiple discharge/recharge cycles.

Procedure. The procedure followed during the single and five-cell ZHG cycle testing was:

- Zinc H<sub>2</sub> Generator Number 2 was tested for 10 cycles in addition to the initial current density cycle. It was discharged at a current density of 20 mA/cm<sup>2</sup> (18.6 ASF) and recharged at 10 mA/cm<sup>2</sup> (9.3 ASF) for the first three cycles and 5 mA/cm<sup>2</sup> (4.6 ASF) for the remaining seven.
- Zinc H<sub>2</sub> Generator Number 3 was used to construct a five-cell Zn H<sub>2</sub> Generator Module (ZHGM). This module was tested for seven cycles. Discharge and recharge current densities for this testing were 10 mA/cm<sup>2</sup> (9.3 ASF).

Results. The results of the single-cell cycle test are presented in Figure 8. Included is both the average cell cycle voltage and the final cell cycle voltages. The data for the single-cell testing was extrapolated by drawing a least-squares straight through to the data to yield the approximate number of cycles that could be expected from the cell. Using the criteria that the last cycle is the cycle when the final cell voltage equals zero, since any further cycles would require power to generate  $H_2$ , over 50 cycles were possible using the ZHG Number 2. The maximum number of cycles for the ZHG can be increased primarily by reducing the depth of discharge (the percent of Zn electrode consumed) from 59% to 10% to 15%. Literature indicates that the number of cycles can be increased from 30 to 50 cycles at 37% Zn utilization to over 1000 cycles at 12.5%.

The results of the five-cell ZHG testing are presented in Figures 9 and 10. The first three cycles were integrated with a single-cell EDC. An additional four cycles were run following the integrated ZHG/EDC testing. The  $\rm H_2$  production rates of the five-cell ZHG Number 3 were within expected accuracy of the theoretical rates of 55.5 scc/min. During the fifth cycle the recharge voltage began to fluctuate, indicating one of the ZHG cells developed an internal leak from the Zn electrode to the  $\rm H_2$  cavity. The module was examined and each cell was individually tested. Cell Number 2 was isolated as the bad cell. The module was reassembled and Cell Number 2 was electrically isolated. The four remaining cells were run for two additional cycles.

## ZHG/EDC Integrated Testing

The ZHG five-cell module and the single-cell EDC were integrated so that  $\rm H_2$  produced by the ZHG was used by the EDC for the  $\rm CO_2$  removal process.

Objective. The objective of the integrated testing was to verify EDC performance at nominal levels using ZHG-produced  $\rm H_2$  at 1.5, the stoichiometric required  $\rm H_2$  flow rate.

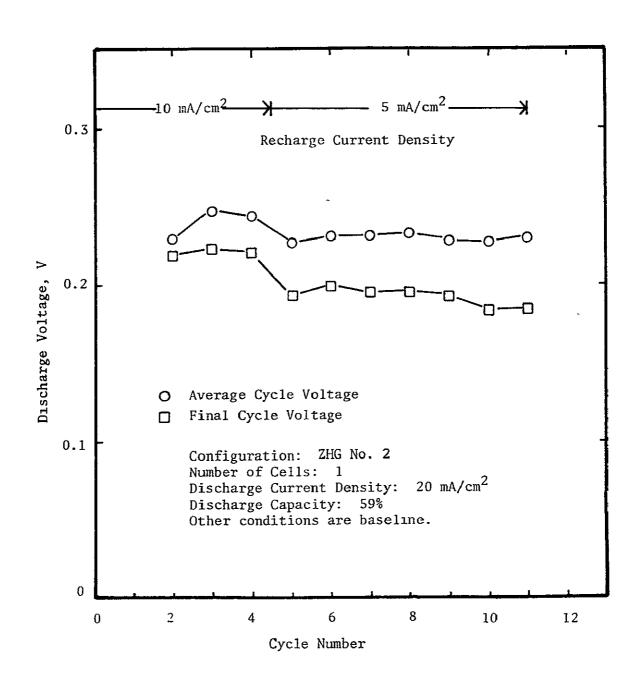


FIGURE 8 SINGLE-CELL CYCLE PERFORMANCE

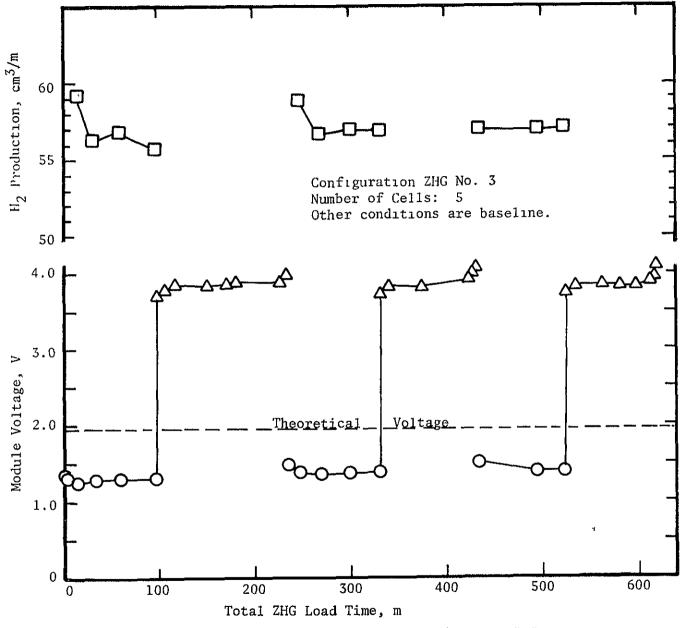


FIGURE 9 ZHG PERFORMANCE FOR INTEGRATED ZHG/EDC TESTING

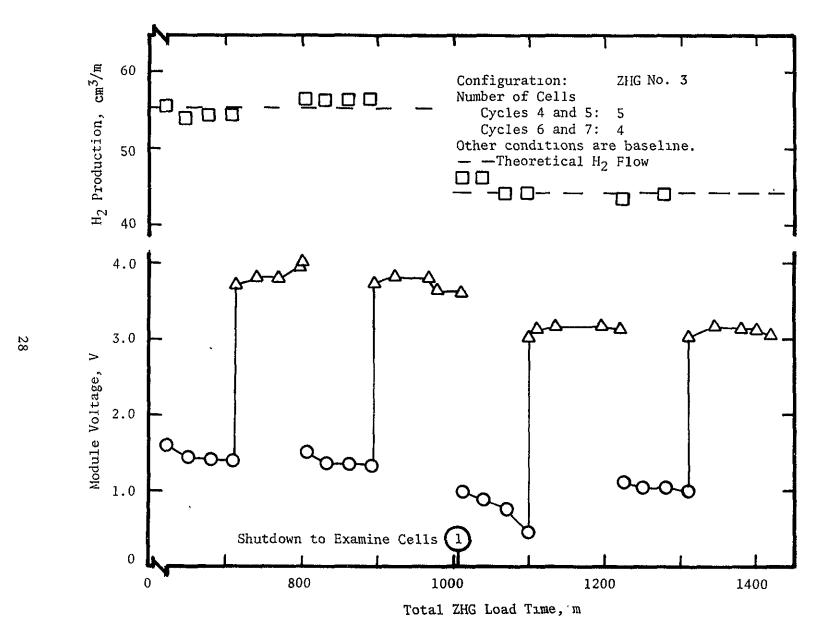


FIGURE 10 ADDITIONAL ZHG MODULE CYCLE TESTING

Procedure. The procedure followed during the integrated ZHG/EDC testing was:

- 1. The EDC was shakedown tested.
- 2. The EDC was integrated with the five-cell ZHG.
- 3. Process air flow rate to the EDC and current to the ZHG were established at baseline conditions. The EDC current density level was set at 21.5 mA/cm<sup>2</sup> (20 ASF) when normal EDC open-circuit voltage (approximately 1.0V) was reached.
- 4. The ZHG and EDC were operated for approximately 90 minutes, at which time the EDC was shut down. The ZHG current flow was reversed, H<sub>2</sub> flow was supplied and the ZHG was recharged at 10 mA/cm<sup>2</sup> (9.3 ASF). Three integrated cycles were performed following this procedure for each cycle.

Results. The EDC single cell was shakedown tested to verify operability prior to integration with the ZHG. During shakedown testing the EDC illustrated a TI of 2.0 kg  $\rm CO_2/kg~O_2$  at an inlet pCO $_2$  level of 400 kN/m $^2$  (3 mm Hg) and a cell voltage of 0.2V.

The results of the three-cycle ZHG/EDC integrated testing are presented in Figure 11. The average H<sub>2</sub> production rate of the ZHG as calculated from the EDC outlet H<sub>2</sub> and CO<sub>2</sub> flow was 56.8 scm /min. The EDC demonstrated an air side TI of 2.45 kg CO<sub>2</sub>/kg O<sub>2</sub> and a H<sub>2</sub> side TI of 2.0 kg CO<sub>2</sub>/kg O<sub>2</sub>. The EDC cell voltage steadily rose during the testing and leveled at 0.29V. The pCO<sub>2</sub> level was held constant at 400 kN/m (3 mm Hg) and the relative humidity (RH) was approximately 65%.

The ZHG dependably produced 1.5 stoichiometric-in-current  $\rm H_2$  gas flow for direct use in a single-cell EDC and, therefore, ZHG/EDC operational feasibility for  $\rm CO_2$  removal was successfully demostrated.

#### Zn/EDC CONCEPT

A block diagram of the Zn/EDC CO<sub>2</sub> removal subsystem as integrated within a PLSS is presented in Figure 12. It depicts the atmosphere revitalization loop, the liquid cooling loop and the controller connections to the various subsystems of the PLSS. The Zn/EDC is the second subsystem in the atmospheric revitalization loop. The inlet process air to the Zn/EDC is warm, moist, debris-free air at a high pCO<sub>2</sub> level. The Zn/EDC places a load on the heat rejection subsystem and requires connections to the PLSS controller.

#### Zn/EDC Process Description

Carbon dioxide is removed from a process air stream as it passes over the cathode of the Zn/EDC in the same way CO<sub>2</sub> is removed in an EDC. The operation of a Zn/EDC occurs in two modes, discharge and recharge. Table 7 summarizes the cell reactions.

30

FIGURE 11 EDC PERFORMANCE FOR INTEGRATED ZHG/EDC TESTING

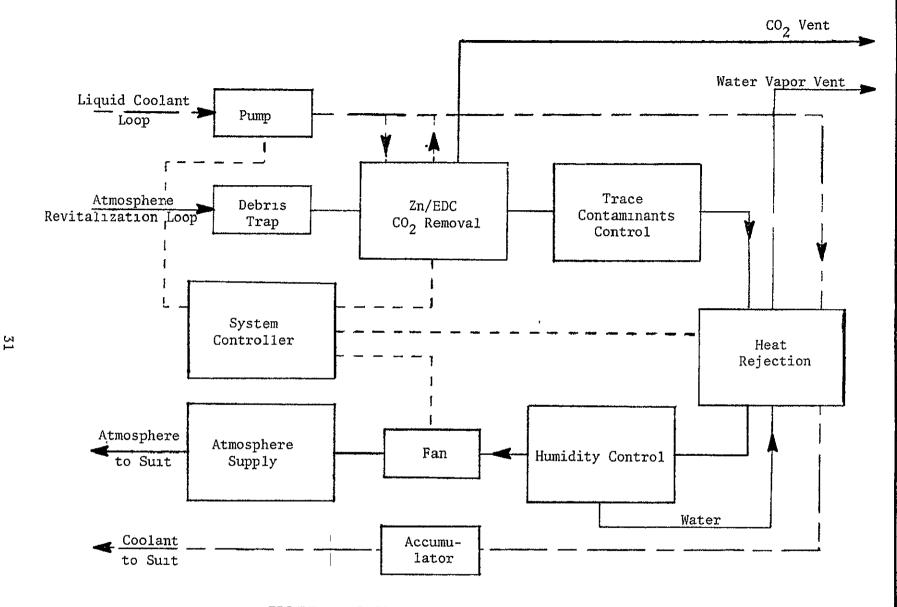


FIGURE 12 PLSS BLOCK DIAGRAM FOR Zn/EDC CONCEPT

# TABLE 7 Zn/EDC ELECTROCHEMICAL AND CHEMICAL DISCHARGE REACTIONS (a)

CATHODE

$$0_2 + 2H_2O + 4e^- = 40H^-$$
 (1)

$$2CO_2 + 4OH^{-} = 2CO_3^{-} + 2H_2O$$
 (2)

ANODE

$$2Zn + 4OH^{-} = 2Zn(OH)_{2} + 4e^{-}$$
 (3)

$$2Zn + 4OH^{-} = 2ZnO + 2H_{2}O + 4e^{-}$$
 (4)

$$2Zn + 2CO_3^{=} = 2ZnCO_3 + 4e^{-}$$
 (5)

$$2CO_3^{=} + 2H_2O = 2CO_2 + 4OH^{-}$$
 (6)

OVERALL

$$2Zn + O_2 + 2CO_2 + 2H_2O = 2Zn(OH)_2 + 2CO_2$$
 (7) (b)

$$2Zn + O_2 + 2CO_2 = 2ZnO + 2CO_2$$
 (8) (c)

$$2Zn + O_2 + 2CO_2 = 2ZnCO_3$$
 (9) (d)

<sup>(</sup>a) Recharge reactions are the reverse reactions of the discharge reactions.

<sup>(</sup>b) Reaction (7) is the sum of reactions (1), (2), (3) and (6).

<sup>(</sup>c) Reaction (8) is the sum of reactions (1), (2), (4) and (6).

<sup>(</sup>d) Reaction (9) is the sum of reactions (1), (2) and (5).

The discharge mode is the CO2 removal mode during which  $O_2$  is reduced in the presence of water to form OH ions. Carbon dioxide is then absorbed into the electrolyte where it reacts with two OH ions to form  $CO_3$  and water. The  $CO_3$  and unreacted OH transfer across the matrix to the Zn anode. Three primary electrochemical reactions could occur at the anode. The Zn metal reacts with OH to form Zn hydroxide  $(Zn(OH)_2)$  or Zn oxide (ZnO) and water. The Zn can also react with  $CO_3$  to form zinc carbonate  $(ZnCO_3)$ . The  $ZnCO_3$  binds the  $CO_2$  in the electrolyte and no  $CO_2$  is evolved. If oxidized Zn ions show a preference toward combining with  $OH_2$  to form  $Zn(OH)_2$  or  $ZnO_3$ ,  $CO_3$  will evolve by the chemical reaction of  $CO_3$  and water, the same as at an EDC anode. The theoretical discharge voltage of the cell is 1.6V and with the feasible operating current density the system will produce electrical power during the discharge mode.

During recharge the Zn salt is reduced back to Zn metal to reform the electrode. The electrochemical process at the recharge anode is similar to the reverse of the discharge cathode mechanism. The OH are oxidized to form  $0_2$ , water and electrons. As in the EDC, the Zn/EDC recharge anode reactions will cause the evolution of  $C0_2$  from the electrolyte until the steady-state  $C0_2$  content of the electrolyte is established. The evolution of  $C0_2$  creates an increased OH concentration of the electrolyte after recharge. The overall recharge process of the Zn/EDC results in the consumption of electrical energy, the production of heat and a partial decrease in the  $C0_2$  content of the electrolyte.

### Hardware

The Zn/EDC is simply an EDC cell with a Zn anode. A schematic of a single cell is presented in Figure 13. A photograph of a Zn/EDC cell is presented in Figure 14. Table 8 contains the Zn/EDC cell components and materials of construction. The Zn anode is fabricated by reducing a mixture of Zn oxidized mercury oxide (2%) onto a silver sheet current collector. This fabrication technique results in a high performance Zn electrode with good recharge capabilities. The cathode is a standard LSI catalyzed screen electrode normally used in EDC construction. The polymer separator film is designed to prevent dendrite formation during recharge and is required for long-term operation. The electrolyte matrix is asbestos. The current collectors are Ni with exmet cavity spacers to provide gas passageways and electrode contact. The cell housing and cooling frames are constructed of injection-molded polysulfone. The cell utilizes internal liquid cooling, adjacent to the cathode gas cavity, to remove the waste heat generated by the electrochemical reactions. Cell sealing is accomplished with flat ethylene propylene gaskets. The Zn/EDC was charged with Cs<sub>2</sub>CO<sub>3</sub> electrolyte initially, but later CsOH was used.

### Process Parameters

The production and consumption rates of the compounds involved in the Zn/EDC electrochemical processes are described by Faraday's Law. The rates for the Zn and  $\theta_2$  consumption, and power and heat generation are given in Equations 3, 8, 4 and 7, respectively, provided in the discussion of the ZHG and the EDC electrochemical processes.

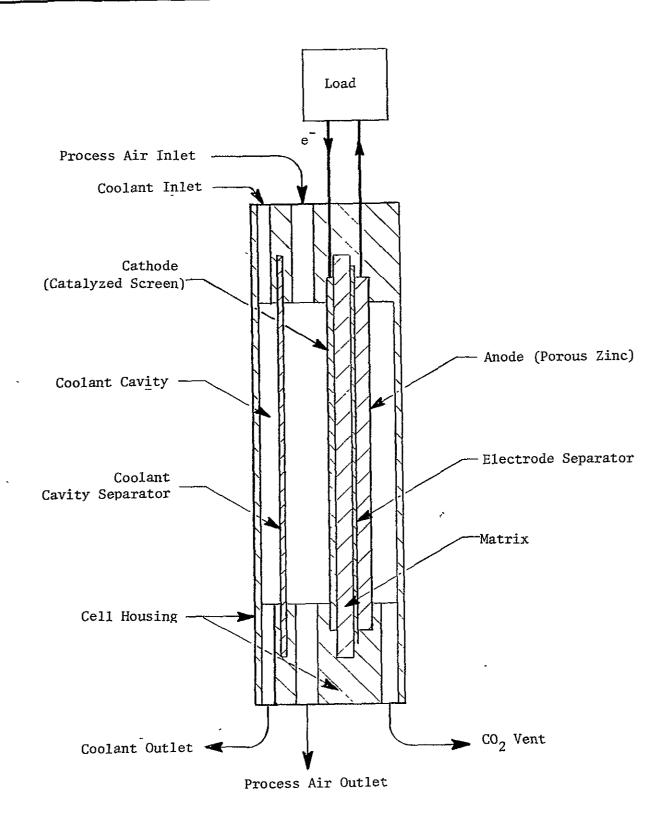


FIGURE 13 Zn/EDC CELL SCHEMATIC

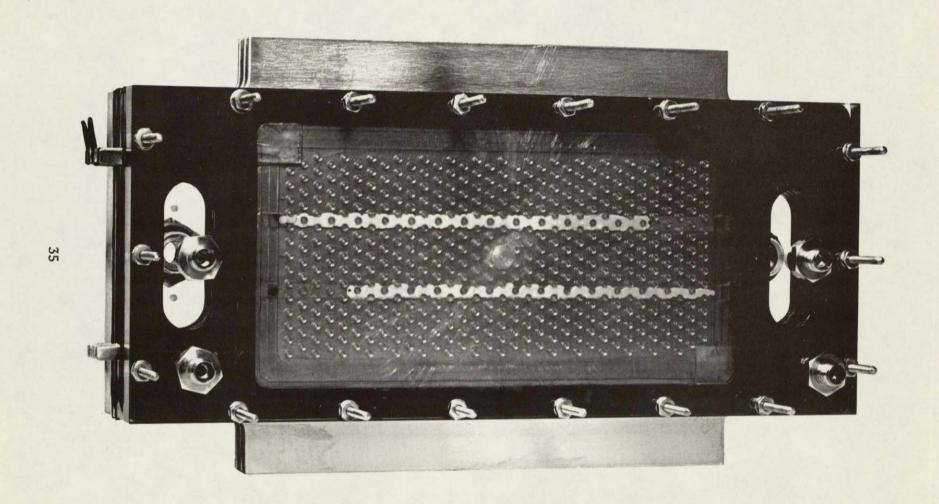


FIGURE 14 LIQUID-COOLED Zn/EDC

### TABLE 8 Zn/EDC CELL COMPONENT CHARACTERISTICS

Active Area, cm<sup>2</sup> (Ft<sup>2</sup>)

Dimensions, cm (In)

Anode (Discharge)

Anode Thickness, cm (In)

Discharge Capacity, A-h

Cathode (Discharge)

Cathode Thickness, cm (In)

Matrix

Matrix Thickness, cm (In)

Electrode Separator

Coolant Cavity Separator

Cell Housing Frames

Air Cavity Height, cm (In)

Anode Cavity Height, cm (In)

Coolant Cavity Height, cm (In)

Gas Cavity Spacers

Current Collectors

Gaskets

227 (0.244)

10.4 x 21.8 (4.1 x 8.6)

Porous Zinc

0.076 (0.030)

12.5

Catalyzed Screen

0.025 (0.010)

Asbestos

0.076 (0.030)

Porous Polypropylene (a)

Polysulfone

Injection-Molded Polysulfone

0.208 (0.082)

0.102 (0.040)

0.165 (0.065)

Nickel 200

Nickel 200

Ethylene Propylene

<sup>(</sup>a) Not used during testing.

### Performance Parameters

The performance of the Zn/EDC can be measured by four parameters: CO<sub>2</sub> removal efficiency, projected cycle life, average cell voltage and recharge current efficiency. Since the Zn/EDC is an internal cell integration of the ZHG and EDC concepts to eliminate the need for H<sub>2</sub>, Zn/EDC performance is evaluated in the same manner previously described. The CO<sub>2</sub> removal efficiency is based on a carbonate mechanism and a TI of 2.75 is equivalent to 100% CO<sub>2</sub> removal efficiency. Electrical efficiency is measured by the average cell voltage. Projected cycle life refers to the number of power-producing discharge cycles for the Zn/EDC. Recharge current efficiency reflects the amount of current required to recharge the cell and regenerate the Zn electrode.

### Ground Support Accessories for Zn/EDC Testing

The GSA used in the Zn/EDC testing is the same test setup (Figure 6) that was used for the EDC testing during the ZHG/EDC integrated test. Only minor modifications to the power controller were made to allow the cell to be recharged.

### Zn/EDC Test Program

The test program was designed to determine if the Zn/EDC concept is operable as a potential PLSS CO<sub>2</sub> scrubber. The test program consisted of two tests, a discharge test and discharge/recharge cycle. The baseline Zn/EDC operating conditions for the test program are presented in Table 9.

### Discharge Test

A single-cell Zn/EDC was discharged at baseline conditions to determine operational feasibility.

 $\underline{\text{Objective}}.$  The objective of the discharge test was to determine if the Zn/EDC would perform the CO  $_2$  removal function.

Procedure. The following procedure was used for the testing:

- Fabricate, assemble and charge the Zn/EDC with Cs<sub>2</sub>CO<sub>3</sub>.
- 2. After integration into the GSA, perform a discharge mode at 21.5 mA/cm<sup>2</sup> (20 ASF).
- 3. After completion of the discharge mode, disassemble Zn/EDC and visually observe the Zn anode.

Results. The result of the Zn/EDC discharge test was that steady-state Zn/EDC operation was not possible. After establishing baseline operating flow conditions and observing the open-circuit terminal voltage to be 1.37V, the current density was set at 21.5 mA/cm<sup>2</sup> (20 ASF). Within one minute the terminal voltage was -1.1V and dropping. After an operator shutdown, startup was again attempted

### TABLE 9 Zn/EDC BASELINE CONDITIONS

Air Flow Rate, m <sup>3</sup> /s (Scfm)  pCO <sub>2</sub> , N/m <sup>2</sup> (mm Hg) Inlet RH, % Inlet Process Air Temperature, K (F) Cell Temperature, K (F) Cooling Water Flow Rate, cm <sup>3</sup> /m Current, A	2.8 ±0.2 x 10 <sup>-4</sup> (0.60 ±0.04) 400 (3) 65 ±5 294 ±3 (70 ±5) 295 ±3 (72 ±5) 500
Discharge Recharge	4.88 4.88
Current Density, mA/cm <sup>2</sup> (ASF)	
Discharge Recharge	21.5 (20) 21.5 (20)
Electrolyte Charge Concentration, % Pressure, kN/m <sup>2</sup> (mm Hg)  Cell Capacity, A-h Capacity Discharge, %	Cs <sub>2</sub> CO <sub>3</sub> 61.5 97.3 ±1.3 (730 ±10) 12.5 45

with very small increases in current, but again the terminal voltage reached negative potentials and the test was terminated. Upon disassembly of the Zn/EDC, no errors in fabrication or modification to the Zn anode were detected that would have caused the resulting performance. It was assumed that the CO content of the electrolyte (i.e., carbonate electrolyte) caused the poor performance and to verify this, a second discharge cycle was planned after a rebuild and charge with CsOH electrolyte.

### Discharge/Recharge

A discharge/recharge test at baseline conditions using CsOH electrolyte was performed to determine if the  ${\rm Cs_2CO_3}$  electrolyte had caused the Zn/EDC not to operate.

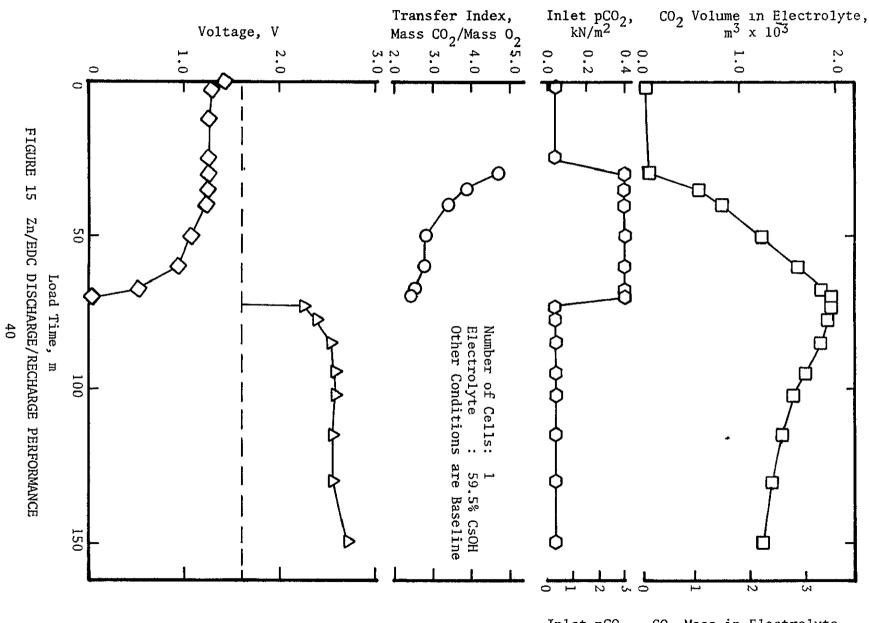
Objective. The objectives of the discharge/recharge test was to verify the ability of the cell to operate in a discharge mode with the CsOH electrolyte, to observe the effects of increased electrolyte CO<sub>3</sub> concentration as CO<sub>2</sub> dissolved into the electrolyte, and to test the regenerability of the Zn/EDC after discharge.

<u>Procedure</u>. The following procedure was followed during the discharge/recharge testing:

- 1. The Zn/EDC was assembled and charged with 59.9% CsOH electrolyte. The cesium ion (Cs $^+$ ) molar concentration was equivalent to the Cs $^+$  concentration of the 61.5% Cs $_2$ CO $_3$  charge used during the discharge testing.
- 2. After integration into the GSA, process air at ambient pCO<sub>2</sub> was introduced into the cell.
- 3. Current density was set at 21.5 mA/cm<sup>2</sup> (20 ASF).
- 4. After operation for 25 minutes, the inlet  $pCO_2$  level was raised to  $400 \text{ kN/m}^2$  (3 mm Hg). Operation was continued until negative potential was reached and automatic shutdown occurred.
- 5. Process air inlet pCO<sub>2</sub> level was decreased to ambient and recharge current density was set at 21.5 mA/cm<sup>2</sup> (20 ASF). Recharge was discontinued when the terminal voltage began rapidly increasing, indicating a change in the recharge electrochemical mechanism.

Results. The results of the Zn/EDC discharge/recharge testing with the CsOH electrolyte are presented in Figure 15. The figure illustrates terminal voltage for both the discharge and recharge modes, the discharge TI, the inlet pCO level of the process air and the CO content of the electrolyte evaluated on a volumetric basis.

After introducing process air flow through the Zn/EDC at ambient pCO $_2$  level, the open-circuit terminal voltage reached 1.43V. Current was applied and was maintained for 30 minutes at the ambient pCO $_2$  level. During this operation, the



Inlet  $pCO_2$ ,  $CO_2$  Mass in Electrolyte, p

average terminal voltage was 1.25V. The pCO $_2$  level was increased to 400 kN/m $^2$  (3 mm Hg) after the initial 30 minutes of testing. With the introduction of the CO $_2$  into the process air stream and its subsequent removal by the Zn/EDC, the electrical performance degraded until, at a load time of 70 minutes, the terminal voltage reached a level of 0.00V and testing was discontinued. The CO $_2$  removal performance was excellent due to the CsOH electrolyte charge. It ranged from the TI of 4.7 and decayed to a point of 2.41 at shutdown. A TI greater than the maximum theoretical of 2.75 was attained since CO $_2$  was removed by OH $^-$  in the electrolyte in addition to OH $^-$  generated by the electrochemical cell cathode reaction.

The recharge mode was performed at 21.5 mA/cm $^2$  (20 ASF) at the ambient inlet air pCO $_2$  level. All other conditions remained constant at baseline. The recharge voltage leveled off at approximately 2.55V. During the recharge mode, CO $_2$  was evolved in the process air stream due to the reversal of current and the CO $_2$  content of the electrolyte. The CO $_2$  evolution at the recharge anode continued throughout the 80 minutes of recharge and illustrated the decreasing evolution rate as expected with decreased CO $_2$  content of the electrolyte.

Based on the results of Zn/EDC testing with CsOH electrolyte, it was concluded that the cell could not perform the designed function using  $Cs_2CO_3$  electrolyte. Additional work beyond the scope of the present program would be required to determine the limiting mechanism and if the cell could be made operable.

### CONCEPT EVALUATION

The ZHG/EDC and the Zn/EDC concepts were evaluated on the basis of total system equivalent launch weight and the actual CO<sub>2</sub> removal system volume for an individual EVA mission. Projected performance and electrochemical module design characteristics for the fully-developed systems were used for the evaluation.

### Design Specifications

The detailed design specifications used in the evaluation are presented in Table 10. The specifications are based on previously completed studies to define Advanced Extravehicular Protective System (AEPS) requirements. (7,8) The specifications include CO<sub>2</sub> removal requirements, the length and frequency of EVA missions and atmospheric data projected for the PLSS air revitalization loop. There are several major differences between the PLSS specifications and those of the primary space vehicle Air Revitalization System (ARS). The CO<sub>2</sub> removal requirement of 0.118 kg/hr (0.26 lb/hr) per man is 2.8 times the ARS CO<sub>2</sub> removal requirement of 0.042 kg/hr (0.092 lb/hr) per man. The low PLSS process air flow rate and small suit volume requires that CO<sub>2</sub> be removed at the same rate that CO<sub>2</sub> is produced; i.e., there is no large volume to damp-out sudden increases in CO<sub>2</sub> production. The high CO<sub>2</sub> removal requirement and the requirement to suddenly increase the CO<sub>2</sub> removal rate to match increased CO<sub>2</sub> production severely impact the size of the ZnDC concepts which are rate-limited processes. Hardware must be designed to meet the highest CO<sub>2</sub> removal rate projected for an EVA mission, as opposed to capacity-limited CO<sub>2</sub> removal concepts which must only be sized for the projected total CO<sub>2</sub> removal requirement.

TABLE 10 PLSS  ${\rm CO}_2$  SCRUBBER DESIGN SPECIFICATIONS

### Crew Data

Number of Crew Metabolic Rates, J/h-Man (Btu/Hr-Man) Average Maximum Sustained Maximum CO <sub>2</sub> Generation Rate, kg/h-Man (Lb/Hr-Man) Average Maximum Sustained Maximum O <sub>2</sub> Consumption, kg/h-Man (Lb/Hr-Man) Average Maximum Sustained Maximum Sustained Maximum Respiratory Quotient Base, Vol. CO <sub>2</sub> Exhaled/Vol. O <sub>2</sub> Inhaled	1 1.27 x 10 <sup>6</sup> (1200) 1.69 x 10 <sup>6</sup> (1600) 3.69 x 10 <sup>6</sup> (3500)  0.118 (0.26) 0.159 (0.35) 0.341 (0.752)  0.088 (0.195) 0.119 (0.262) 0.256 (0.564)  0.97
Mission Data	
Mission Length Maximum, h Nominal, h Frequency of Mission Maximum/Day Nominal/Day Maximum Number of EVA Atmosphere Data	12 4 to 8 3 1 250
	0.4.0.0.00.4.13
Operational Gravity Range, N/kg (g) Total Pressure, kN/m <sup>2</sup> (Psi) Suit Gas Composition Pure O <sub>2</sub> , kN/m <sup>2</sup> (Psi) O <sub>2</sub> -N <sub>2</sub> Mixture, kN/m <sup>2</sup> (Psi)	0 to 9.8 (0 to 1) 48 to 55 (7 to 8) 48 to 55 (7 to 8) 48 to 55 (7 to 8)
CO <sub>2</sub> Partial Pressure  Nominal, N/m <sup>2</sup> (mm Hg)  Maximum, N/m <sup>2</sup> (mm Hg)  Emergency Maximum, N/m <sup>2</sup> (mm Hg)  O <sub>2</sub> Partial Pressure	533 (4.0) 1000 (7.5) 2000 (15.0)
Nominal, kN/m <sup>2</sup> (Psi) Ventilation Inlet Flow Rate, m <sup>3</sup> /s (Cfm) Nominal	25.5 to 55.2 (3.7 to 8) $2.36 \times 10^{-3} (5.0)$
Emergency	$2.36 \times 10^{-3} (5.0)$ $4.25 \times 10^{-3} (9.0)$

continued-

### TABLE 10 - continued

Inlet Temperature, K'(F)	
Nominal	283 to 294 (50 to 70)
Emergency	283 (50)
Inlet Dew Point, K (F)	
Minimum	277 (40)
Nominal	280 (45)
Maximum	289 (60)
Relative Humidity, %	70 to 40
Liquid Coolant Transport Loop Data	
Flow Rate, kg/m (Lb/Hr) Temperature, K (F)	109 (240)
Minimum	277.4 (40)
Maximum	288.6 (60)

### System Characteristics

The performance and electrochemical module design characteristics used for the evaluation are presented in Tables 11 and 12, respectively, for the ZHG/EDC concept, and Tables 13 and 14, respectively, for the Zn/EDC system. The performance characteristics include number of cells, projected cell voltage and current density, power and heat generation, and gas generation. The systems' physical characteristics include module and accessory power weight and volume, both during the EVA mission and during recharge. The system designs were based on an eight-hour EVA mission, a 15-hour regeneration period and a one-hour period to remove the system for recharging and replace it after recharging is complete.

The ZHG/EDC concept would have an EVA system weight of 37.8 kg (83.3 lb) and a volume of 0.030 m<sup>3</sup> (1.07 ft<sup>3</sup>) which include both the module and accessories. The Zn/EDC system has an EVA system weight of 26.7 kg (58.8 lb) and a volume of 0.024 m<sup>3</sup> (0.85 ft<sup>3</sup>).

### System Evaluation

Table 15 presents a comparison of the ZHG/EDC and Zn/EDC  ${\rm CO}_2$  removal concepts on the basis of total equivalent launch weight. The two Zn concepts are not completely regenerable  ${\rm CO}_2$  removal methods since  ${\rm CO}_2$  is vented to space vacuum and  ${\rm O}_2$  is consumed in the  ${\rm CO}_2$  removal process. The assumptions used in the equivalent weight estimates are presented in Table 16. The equivalent weight for both ZnDC concepts is approximately the same. The lower module weight associated with the Zn/EDC concept, since only one electrochemical module is required, is offset by the power required for the recharge system. The Zn/EDC concept, however, does have a lower EVA volume than the ZHG/EDC, making it more attractive for the application.

A comparison of the ZnDC concepts to alternate PLSS  $CO_2$  removal concepts (8,9) was completed on the basis of total system equivalent launch weight and EVA mission volume. Figure 16 shows total system equivalent launch weight per man for six candidate  $CO_2$  removal systems. The Zn/EDC concepts have a lower system equivalent launch weight than the LiOH or vacuum desorbed solid amine systems for total EVA mission durations greater than 400 hours. The regenerable carbonate and regenerable hydroxide systems, however, have a lower equivalent weight than the two ZnDC concepts. Figure 17 shows the EVA mission volume associated with both ZnDC concepts. The EVA mission volumes include the volumes associated with excess  $O_2$  that must be stored for consumption in the  $CO_2$  removal process.

Although both ZnDC concepts have a lower equivalent launch weight than the standard LiOH method for increased EVAs, they offer no launch weight or EVA mission volume advantages over the regenerable carbonate and hydroxide systems. In addition, H<sub>2</sub> is present in the ZHG/EDC system, which presents a possible safety hazard. The Zn/EDC concept has not been shown operationally feasible. On the basis of this evaluation, further work on the ZnDC PLSS CO<sub>2</sub> removal concepts is not recommended at this time.

	Discharge		Recharge
ZHG Performance Characteristics	Nominal	Peak	
Number of Cells	24	24	24
Active Area Per Cell, $cm^2$ (Ft <sup>2</sup> )	976 (1.05)	976 (1.05)	976 (1.05)
Current Density, mA/cm <sup>2</sup> (ASF)	10 (9.3)	14.0 (13.0)	5.33 (4.96)
Current, A	9.76	13.6	5.20
Average Cell Voltage, V	0.23	0.19	0.47
H <sub>2</sub> Production Rate, kg/h (Lb/Hr)	0.00874 (0.0193)	0.0122 (0.0268)	-0.00466 (-0.0103)
Current Efficiency, %	100	100	90
Power Generated, W	53.9	62.0	-58.7
Heat Generated, J/s (BTU/Hr)	37.0 (127)	64.6 (221.0)	15.1 (51.6)
Capacity Discharge, %	30	TBD	and the term
Water Consumed, kg/h (Lb/Hr)	0.079 (0.173)	0.110 (0.242)	-0.038 (-0.083)
Time of Operation, h <sup>(a)</sup>	8	TBD	15
Number of Cells Active Area Per Cell, cm <sup>2</sup> (Ft <sup>2</sup> ) Current Density, mA/cm <sup>2</sup> (ASF) Current, A Average Cell Voltage, V CO <sub>2</sub> Removal Efficiency, %	16 453 (0.488) 21.5 (20) 9.76 0.40 92	16 453 (0.488) 30 (27.9) 13.6 0.2 89	
Transfer Index, kg $CO_2/kg O_2$ (Lb $CO_2/lb O_2$ ) $CO_2$ Removal Rate, kg/h (Lb/Hr)	2.54 (2.54) 0.119 (0.262)	2.44 (2.44) 0.159 (0.35)	
Power Generated, W	62.5	43.5	
Heat Generated, J/s (BTU/Hr)			
Sensible Latent O <sub>2</sub> Consumed, kg/h (Lb/Hr) H <sub>2</sub> Consumed, kg/h (Lb/Hr) Water Produced, kg/h (Lb/Hr) Time of Operation, h <sup>(a)</sup>	130 (44.3) 39.3 (134) 0.047 (0.103) 0.0058 (0.013) 0.058 (0.128) 8	224.1 (766) 49.4 (169) 0.0650 (0.143) 0.0081 (0.018) 0.073 (0.161) TBD	

<sup>(</sup>a) For sizing purposes, 8 hours of operation at nominal conditions was assumed.

### TABLE 12 ZHG/EDC SUBSYSTEM CHARACTERISTICS

#### ZHG Module (ZHGM) (a) ZHG Cell Mass/Cell, kg (Lb) 0.509(1.12) $2.05 \times 10^{-4} \ (7.25 \times 10^{-3})$ Volume/Cell, m<sup>3</sup> (Ft<sup>3</sup>) 12.2 (26.9) Mass/24 Cells, kg (Lb) $4.92 \times 10^{-3} (0.174)$ Volume/24 Cells, m<sup>3</sup> (Ft<sup>3</sup>) ZHG End Plates and Isolation Plates 3.73 (8.2) Mass, kg (Lb) $3.1 \times 10^{-3} (0.109)$ Volume, $m^3$ (Ft<sup>3</sup>) ZHGM Mass, kg (Lb) 15.9 (35.0) $8.02 \times 10^{-3} (0.283)$ ZHGM Volume, $m^3$ (Ft<sup>3</sup>) $0.247 \times 0.247 \times 0.124$ Basic Configuration, m (In) $(9.72 \times 9.72 \times 4.9)$ Power, W(b) -53.9 EDC Module (EDCM) (c) EDC Cell 0.776 (1.71) Mass/Cell, kg (Lb) $8.04 \times 10^{-4} (2.84 \times 10^{-2})$ Volume/Cell, $m^3$ (Ft<sup>3</sup>) 12.4 (27.3) 1.29 x $10^{-2}$ (0.454) Mass/16 Cells, kg (Lb) Volume/16 Cells, $m^3$ (Ft<sup>3</sup>) EDC End Plates and Isolation Plates 6.43 (14.17) Mass, kg (Lb) $5.35 \times 10^{-3} (1.89 \times 10^{-1})$ Volume, $m^3$ (Ft<sup>3</sup>) 18.86 (41.5) EDCM Mass, kg (Lb) EDCM Volume, m<sup>3</sup> (Ft<sup>3</sup>) 0.0182 (0.643) $0.26 \times 0.28 \times 0.26$ Basic Configuration, m (In) $(10.2 \times 11.2 \times 10.2)$ -62.5Power, W EVA Accessories 3.05 (6.72) Mass, kg (Lb) $3.90 \times 10^{-3} (0.14)$ Volume, $m^3$ (Ft<sup>3</sup>) Power, W ZHG/EDC Subsystem Mass, kg (Lb) 37.8 (83.3) $3.0 \times 10^{-2} (1.07)$ Volume, $m^3$ (Ft<sup>3</sup>) Power, W -111.4

<sup>(</sup>a) ZHGM sizing is based upon ZHG build of 0.182 cm (0.072 in) anode, 0.026 cm (0.010 in) matrix and separator, 0.013 cm (0.005 in) cathode, and 0.052 cm (0.020 in) spacer.

<sup>(</sup>b) Power generated is represented by a negative number.

<sup>(</sup>c) EDCM sizing is based upon AEDCM design.

<sup>(</sup>a) For sizing purposes, 8 hours of operation at nominal conditions was assumed.

### TABLE 14 Zn/EDC SUBSYSTEM CHARACTERISTICS

## Zn/EDC Module (Zn/EDCM) (a)

Power, W

```
Zn/EDC Cell
          Mass/Cell, kg (Lb)
Volume/Cell, m<sup>3</sup> (Ft<sup>3</sup>)
                                                                   1.074 (2.37)
8.04 x 10<sup>-4</sup> (2.84 x 10<sup>-2</sup>)
          Mass/16 Cells, kg (Lb)
Volume/16 Cells, m<sup>3</sup> (Ft<sup>3</sup>)
                                                                   17.18 (37.85)
                                                                   0.013 (0.454)
     Endplates and Insulation Plates
                                                                   ^{6.43}_{5.35} \times ^{(14.17)}_{10^{-3}} \times ^{(1.89}_{10^{-1}})
          Mass, kg (Lb)
          Volume, m<sup>3</sup> (Ft<sup>3</sup>)
     Zn/EDCM Mass, kg (Lb) \rm Zn/EDCM Volume, m^3 (Ft^3)
                                                                   23.61 (52.0)
                                                                   0.0182(0.643)
     Basic Configuration, m (In)
                                                                   0.26 \times 0.29 \times 0.26
                                                                   (10.2 \times 11.2 \times 10.2)
     Power, W(b)
                                                                   -109.3
     EVA Accessories
         Mass, kg (Lb)
Volume, m (Ft<sup>3</sup>)
                                                                   3.1 (6.82)_{3}
5.75 x 10<sup>-3</sup> (0.203)
          Power, W
Zn/EDC Subsystem
    Mass, kg (Lb)
                                                                   26.7 (58.8)
    Volume, m^3 (Ft<sup>3</sup>)
                                                                   0.0240 (0.85)
```

-104.3

<sup>(</sup>a) Zn/EDC sizing is based upon Advanced Electrochemical Depolarized Concentrator (AEDCM) design with the replacement of the anode with the required amount of zinc metal, 317.5 g/cell.

<sup>(</sup>b) Power generated is represented by negative number.

TABLE 15 EQUIVALENT LAUNCH MASS OF CANDIDATE CO2 REMOVAL SUBSYSTEMS

	ZHG/EDC, kg (Lb)	Zn/EDC, kg (Lb)
Basic System		
Modules Accessories Total	34.75 (76.6) 3.05 (6.72) 37.80 (83.3)	23.6 (52.0) 3.1 (6.83) 26.7 (58.8)
Expendables		
O <sub>2</sub> Water CO <sub>2</sub>	0.093/h (0.205/Hr) -0.052/h (-0.115/Hr) (a) 0.097/h (0.214/Hr)	0.047/h (0.104/Hr) -0.005/h (-0.0011/Hr) 0.085/h (0.187,Hr)
CO <sub>2</sub> Removal Penalty (Primary Vehicle)	0	6.4 (14.1)
Heat Rejection Penalty		
Modules Accessories Total	24.3 (53.5) 0.6 (1.32) 24.9 (54.9)	17.0 (37.5) 0.6 (1.32) 17.6 (38.8)
Recharge System	11.4 (25.1)	11.4 (25.1)
Recharge Power Penalty		
Modules Accessories Total	15.7 (34.6) 4.0 (8.82) 19.7 (43.4)	44.7 (98.5) 4.0 (8.82) 48.7 (107)
Recharge Heat Rejection Penalty		
Modules Accessories Total	1.3 (2.87) 1.3 (2.87) 2.6 (5.73)	2.8 (6.17) 1.3 (2.87) 4.1 (9.04)
Total Equivalent Launch Mass, kg/Man (Lb/Man)	96.4 + 0.138/h (212.3 + 0.304/Hr)	114.9 + 0.127/h (253.1 + 0.280/Hr)

Water produced for use on primary vehicle. Water saved as  $\mathbf{O}_2$  regenerated on board primary vehicle.

### TABLE 16 EQUIVALENT WEIGHT COMPARISON ASSUMPTIONS

- 1. An EVA mission is defined as one man for eight hours of activity.
- The comparison was based upon one EVA mission-day.
- 3. The allowable system regeneration time is 15 hours.
- 4. A regenerable ice pack concept is used for EVA mission heat rejection and the penalties associated are 0.0151 kg/W-h (0.0097 lb/BTU) and 1.94 x  $10^{-5}$  m<sup>3</sup>/W-h (2.0 x  $10^{-4}$  ft<sup>3</sup>/BTU).
- 5. The power penalty for regeneration at the primary space vehicle is 0.268 kg/W (0.591 lb/W).
- 6. The heat rejection penalty for regeneration at the primary space vehicle is 0.0837 kg/W (0.054 lb/BTU/hr) for heat rejected directly to liquid coolant and 0.199 kg/W (0.128 lb/BTU/hr) for heat rejected to cabin air.
- 7. The penalty associated with removing  $\rm CO_2$  from the primary space vehicle atmosphere is 34.4 kg/kg  $\rm CO_2/day$  (1b/1b  $\rm CO_2/day$ ) which assumes an Electrochemical Depolarized  $\rm CO_2$  Concentration.
- 8. The penalty associated with  $O_2$  consumption during an EVA is 2 kg/kg  $O_2$  consumed (2 lb/lb  $O_2$ ), which is 1 kg  $O_2$ /kg  $O_2$  consumed + 1 kg of container/kg  $O_2$  consumed (1 lb  $O_2$ /lb  $O_2$  + 1 lb container/lb  $O_2$ ). The  $O_2$  bottle volume required for an EVA is 2.77 x  $10^{-3}$  m<sup>3</sup>/kg  $O_2$  (0.0444 ft<sup>3</sup>/lb  $O_2$ ).
- 9. The penalty for loss of  $CO_2$  vented to vacuum during an EVA is 0.82 kg/kg  $CO_2$  lost (0.82 lb/lb  $CO_2$  lost).
- 10. Water produced by the EDC is available for use on board the primary space vehicle at a saving of 1 kg/kg water produced (1 1b/1b water).
- 11. O<sub>2</sub> generated during the Zn/EDC recharge is available for spacecraft usage at a savings of 0.126 kg/kg O<sub>2</sub> generated (0.126 lb/lb O<sub>2</sub>).

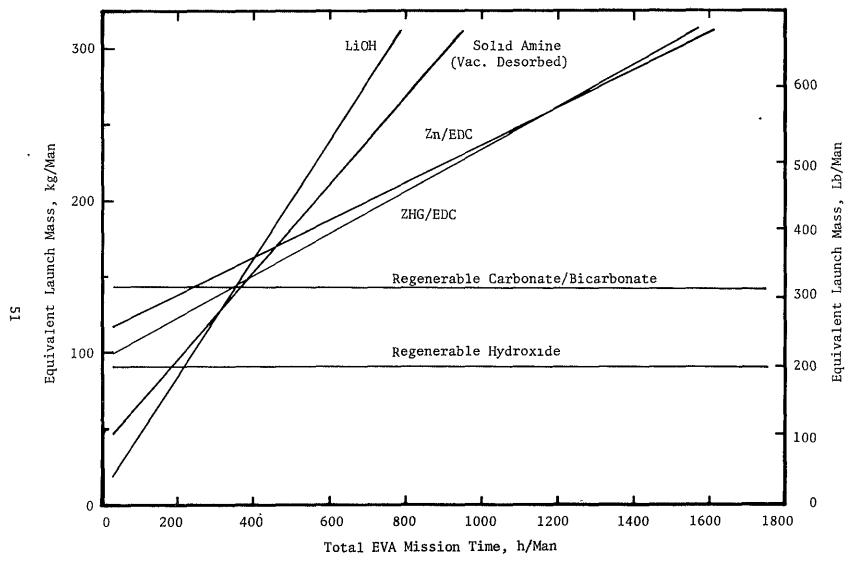


FIGURE 16 LAUNCH MASS COMPARISON OF CANDIDATE PLSS CO<sub>2</sub> REMOVAL SYSTEMS

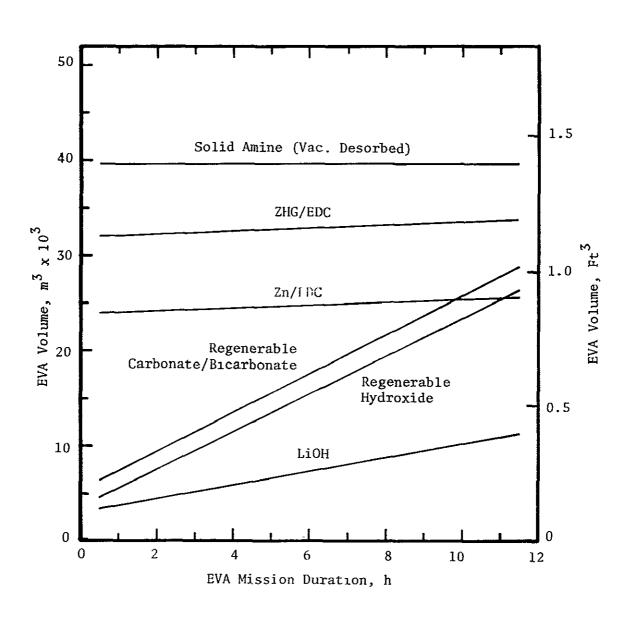


FIGURE 17 EVA MISSION VOLUME COMPARISON OF CANDIDATE PLSS  $\operatorname{CO}_2$  REMOVAL SYSTEMS

#### CONCLUSIONS

The following conclusions are a direct result of the ZnDC evaluation:

- 1. The ZHG/EDC concept is a regenerable method for removing CO<sub>2</sub> from air. The ZHG/EDC concept, however, is not a competitive regenerable method for the PLSS application. Excessive EVA volume (3.0 x 10<sup>-2</sup> m (1.07 ft<sup>3</sup>)) does not compare with the eight-hour EVA<sub>3</sub>volumes for the regenerable carbonate concept<sub>2</sub>(2.17 x 10<sup>-2</sup> (0.766 ft<sup>3</sup>)) or the regenerable hydroxide concept (1.94 x 10<sup>-2</sup> (0.685 ft<sup>3</sup>)). Expendables cause the ZHG/EDC subsystem equivalent launch mass to rapidly increase as the total EVA time increases.
- 2. The potential Zn/EDC concept is not a competitive regenerable method for the CO<sub>2</sub> scrubber subsystem within a PLSS<sub>2</sub> The Zn/EDC results in only slightly larger EVA volumes (2.51 x 10<sup>-2</sup> m<sup>3</sup> (0.886 ft<sup>3</sup>)) than the regenerable carbonate and hydroxide concepts for an eight-hour EVA mission, but the Zn/EDC's equivalent launch mass is always larger than the hydroxide subsystem and excedes the carbonate/bicarbonate subsystem after only 240 hours. In addition, the Zn/EDC concept has not been experimentally proven feasible as a CO<sub>2</sub> scrubber.
- 3. No additional development effort should be directed toward the improvement of the ZHG/EDC or Zn/EDC CO<sub>2</sub> removal concepts for PLSS application since ZnDC launch weights and volumes are not competitive with alternate CO<sub>2</sub> removal methods.

### RECOMMENDATIONS

Development efforts should be directed towards potential PLSS  ${\rm CO}_2$  scrubbers which have the following features:

- Passive CO<sub>2</sub> absorption
- 2. No expendables
- 3. Capacity-limiting CO<sub>2</sub> removal process for efficient absorption at peak CO<sub>2</sub> production rates<sup>2</sup>
- 4. Efficient operation at low air flow rates and subatmospheric pressures
- 5. Short regeneration times
- 6. Regeneration which directly integrates with a CO<sub>2</sub> reduction subsystem to eliminate primary space vehicle CO<sub>2</sub> removal penalties

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